

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 211 289 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
05.06.2002 Bulletin 2002/23

(51) Int Cl.7: C08L 53/00, C08L 23/10

(21) Application number: 00126051.2

(22) Date of filing: 29.11.2000

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(71) Applicant: Borealis GmbH
2323 Schwechat-Mannswörth (AT)

(72) Inventor: The designation of the inventor has not yet been filed

(74) Representative: VA TECH Patente GmbH & Co
Stahlstrasse 21 a
4020 Linz (AT)

(54) Polyolefin compositions with improved properties

(57) The invention relates to polyolefin compositions with good impact strength and transparency comprising

- 85 - 98 wt% based on the total weight of the composition of a heterophasic propylene/α-olefin copolymer comprising a polymer or copolymer of propylene and an α-olefin with 0-15 mol% of the α-olefin as matrix polymer and a propylene/α-olefin rubber copolymer comprising 20 -80 mol% of the α-olefin and
- 15 - 2 wt% based on the total weight of the com-

position of an ethylene homopolymer or an ethylene/α-olefin copolymer, the α-olefin in the ethylene copolymer having 4 - 10 carbon atoms, the ethylene homo- or copolymer having a density lower than 0,925 g/m³.

processes for producing these compositions and their use. The compositions are particularly useful for food packaging, especially for deep freezing applications.

Description

[0001] The invention relates to polyolefin compositions with improved impact strength and improved optical properties. More particularly the invention relates to polyolefin compositions, especially polypropylene compositions with improved impact strength at temperatures below room temperature, especially at temperatures below 0°C, having improved optical properties, especially higher transparency and lower haze.

5 The compositions of the inventions are particularly useful for packaging applications, especially for food packaging for deep freezing application.

10 **Background of the invention**

[0002] Polypropylene homopolymers are widely used in packaging applications. Polypropylene homopolymers show balanced properties and are cheap, easily decomposable polymers, but they show poor transparency and low impact strength.

15 It has been suggested to improve the poor optical properties and the impact strength of polypropylene homopolymers by adding nucleating agents and/or clarifiers. Suitable nucleating agents are for example talcum, disorbitol, organic phosphates and the like.

Nevertheless the desired properties of propylene homopolymers cannot be improved to the extent desired, namely to show high impact strength at low temperatures.

20 [0003] Compositions with improved impact strength and improved optical properties are for example propylene/α-olefin random copolymers, wherein the α-olefin is ethylene or an α-olefin with 4 - 10 carbon atoms. Although transparency is higher and impact strength is improved considerably at ambient temperature, impact strength at lower temperature, i.e. 0°C and below is still not satisfying. Propylene/α-olefin random copolymers have a ductile to brittle transition temperature between -5°C and 5°C depending on the monomer content and therefore impact strength at lower temperatures is still very poor.

25 [0004] To improve the impact strength at lower temperatures heterophasic polymer compositions have been suggested. Heterophasic polymers are polymers having a matrix phase (phase 1) and a second phase. The matrix phase is usually a polypropylene homopolymer or polypropylene/α-olefin copolymer phase and the second phase is usually a propylene/α-olefin rubber polymer.

30 The polymers of the second phase have low glass transition temperatures, usually below -30°C. Therefore impact strength of such heterophasic systems is rather satisfying, even for deep freezing applications. A major drawback is the poor transparency due mostly due to big rubber particles in the heterophasic system.

[0005] Several attempts have been made to improve the transparency of heterophasic polymer systems.

35 [0006] EP-B 0 373 660 discloses heterophasic polymer systems with improved impact strength and improved transparency an elastomeric propylene/ethylene as matrix phase and a phase 2 being propylene/α-olefin rubber, wherein the intrinsic viscosity ratio between phase 1 and phase 2 has to be a defined value, namely 0.2. Therefore the heterophasic system of the disclosure of EP B 0 373 660 is restricted to very special combinations of phase 1 and 2 polymers.

40 [0007] EP-A 0 814 127 discloses embrittlement resistant polyolefin compositions and flexible articles thereof based on propylene homopolymers or propylene/α-olefin copolymers and elastomeric copolymers of ethylene with propylene or butene-1. The elastomeric copolymers enhance the flexibility without affecting the clarity of the polymer composition, which is not at least satisfying for packaging applications, although these compositions are claimed to be used for the production of medical articles and food packaging material.

45 [0008] EP B 0 593 221 discloses polypropylene resin compositions comprising polypropylenes of defined MFR and ethylene/α-olefin copolymers with good balance between impact strength and rigidity and high moldability useful for automotive parts. These compositions do not have good optical properties, especially low transparency and high haze.

Object of the invention

[0009] It is an object of the invention to provide polypropylene compositions for packaging applications with improved impact strength at ambient and low temperatures having improved optical properties, especially good transparency and low haze.

50 A further object of the invention is a process for producing polypropylene compositions for packaging applications with improved impact strength at low temperatures and good optical properties.

It is still a further object of the invention to provide articles made of these polypropylene compositions useful for packaging applications, especially for food packaging for deep freezing applications.

Brief description of the invention

[0010] The object of the invention has been solved by providing heterophasic polymer systems which are modified by a modifier which shows improved impact strength as well as improved optical properties.

5 [0011] The invention therefore relates to polyolefin compositions with good impact strength and transparency comprising

10 a) 85 - 98 wt% based on the total weight of the composition of a heterophasic propylene/α-olefin copolymer comprising a polymer or copolymer of propylene and an α-olefin with 0-15 mol% of the α-olefin as matrix polymer and a propylene/α-olefin rubber copolymer comprising 20 -80 mol% of the α-olefin

b) 15 - 2 wt% based on the total weight of the composition of an ethylene homopolymer or an ethylene/α-olefin copolymer, the α-olefin in the ethylene copolymer having 4 - 10 carbon atoms, the ethylene homo-or copolymer having a density lower than 0,925 g/m³.

15 Detailed description of the invention

[0012] Component a) is preferably a heterophasic propylene/α-olefin copolymer comprising a polymer or a copolymer of propylene with 0 - 15 mol% of an α-olefin as matrix polymer (phase 1 polymer) and a propylene/α-olefin rubber copolymer comprising 20 - 80 mol% of the α-olefin.

20 [0013] Preferably the molecular weight of the propylene/α-olefin rubber is equal or lower than the molecular weight of the propylene homopolymer resp. the polypropylene/α-olefin copolymer.

[0014] The heterophasic polymer of component a) may be produced by multistage process polymerisation of polypropylene or polypropylene and α-olefin such as bulk polymerisation, gas phase polymerisation, slurry polymerisation, solution polymerisation or combinations thereof using conventional catalysts. Those processes are well known to one skilled in the art.

25 A preferred process is a combination of a bulk slurry loop reactor(s) and gas phase reactor(s). The matrix polymer can be made either in loop reactors or in a combination of loop and gas phase reactor.

The polymer produced in this way is transferred into another reactor and the propylene/α-olefin rubber is polymerised. Preferably this polymerisation step is done in a gas phase polymerisation.

30 A suitable catalyst for the polymerisation of the heterophasic copolymer is any stereospecific catalyst for propylene polymerisation which is capable of polymerising and copolymerising propylene and comonomers at a temperature of 40 to 110°C and at a pressure from 10 to 100 bar. Ziegler Natta catalysts as well as metallocene catalysts are suitable catalysts.

[0015] One skilled in the art is aware of the various possibilities to produce such heterophasic systems and will simply find out a suitable procedure to produce suitable heterophasic polymer systems which are used in the present invention.

35 [0016] The matrix polymers of the heterophasic polymers of component a) may have a ratio of matrix polymer (polymer of phase 1) to polymer of phase 2 of about 97 : 3 to 80 : 20, preferably 95 : 5 to 90 : 10.

The heterophasic polymer shows a melt flow rate of about 0.1 to 200g/10 min, preferably 0,2 to 50g/10 min, more preferable 0.3 to 20 g/10 min according to ISO 1133. The ethylene content of the matrix polymer may be up to 7 mol% and the overall ethylene content of the heterophasic polymer of component a) may be up to 30 mol%, preferably up to 15 mol %.

[0017] Component b) is an ethylene homopolymer or an ethylene/α-olefin copolymer the α-olefin having 4 - 10 carbon atoms.

45 For example component b) may be a low density ethylene homopolymer or a copolymer of ethylene with for example vinylacetate or butylacrylate or the like. The amount of component b) is 2 - 15 wt% based on the total weight of the composition, preferably 3 - 10 wt%, most preferably 4 - 7 wt%.

[0018] Preferably the density of the low density ethylene homo- or copolymer (component b)) is lower than 0.925g/cm³ according to ISO 1183. More preferably the density of the low density ethylene homo- or copolymer is lower than 0.920g/cm³. Most preferably the density is 0.890 - 0,920 g/cm³.

50 [0019] Preferably the ethylene-homo- or copolymer (component b)) should have a substantially equal or lower melt flow rate (MFR) than the heterophasic polymer of component a) under melting and blending conditions. Those ethylene homo- or copolymers may be produced in a high pressure tubular process or in a high pressure autoclave process. Alternatively, a linear low density type ethylene copolymer may be produced in a low pressure process typically with a Ziegler type catalyst. Further the polymers of component b) may be produced using a metallocene catalyst. The polymers of component b) produced by using metallocene catalysts are typically elastic copolymers of ethylene and butene or octane having a density of preferably 0.890 - 0,915g/cm³.

[0020] The compositions of the present invention may further comprise conventional additives, such as antioxidants, stabilisers, acid scavengers, clarifying agents, coloring agents, anti-UV agents, nucleating agents, antistatic agents,

slip/mould release agents, fillers, like nanofillers, etc. Typically these additives may be present at less than 2 wt% each, more preferably less than 0.5 wt% relative to the total weight of the composition.

[0021] Examples of such conventional additives include Irganox 1010 and Irgafos 168 (commercially available stabilizers from Ciba Speciality Chemicals), calcium stearate and synthetic hydrotalcite (e.g. DHT-4A from Kyowa Chemical Industry) and 1,2:3,4-di(ethylbenzylidene)sorbitol - EBDS (e.g. NC-4 from Mitsui Toatsu and 1,3:2,4 bis(3,4-dimethylbenzylidene)sorbitol -DMBDS (e.g. Millad 3988 from Milliken Chemicals).

[0022] The polypropylene composition of the present invention is preferably clarified. Clarified polypropylenes can be produced for example by adding clarifying or nucleating agents, for examples sorbitol derivatives such as EDBS, MDBS (1,3:2,7-di(methylbenzylidene)sorbitol and DMDBS, phosphate salts, such as for example sodium 2,2'-methylenebis(4,6-di-tertiarybutylphenyl)phosphate, polyvinylcyclohexane etc. Typically such clarifying or nucleating agents may result in haze levels after injection moulding of lower than 60%, preferably lower than 40% in 2 mm injection moulding sheets.

[0023] The polyolefin compositions of the present invention are produced by mixing the heterophasic polymer of component a) with component b) optionally adding conventional additives and/or stabilisers and/or fillers.

[0024] Preferably, mixing is done by melt blending in an extruder or another melt blending unit, preferably in a twin screw extruder usually followed by pelletisation.

The components may be melt blended as such, or melt blending can be done in the presence of a peroxide component for increasing the melt flow rate of the composition. Then the peroxide, preferably an organic peroxide, which is suitable for degradation of polypropylene (visbreaking) is fed to the blending unit together with components a) and b) or the peroxide may be fed separately into the melt blending unit.

[0025] The compositions of the present invention show improved impact strength, especially at temperatures below 0°C and improved optical properties, especially high transparency and low haze.

[0026] The polypropylene composition of this invention can be further converted to an end product by using normal conversion techniques, such as injection moulding, compression moulding, blow moulding (extrusion or injection stretch blow moulding), extrusion (film, sheet, pipe, tuber, profile extrusion), film blowing, thermoforming and the like. Preferably end products are packaging containers made by injection moulding, blow moulding or thermoforming, or packaging films made by film extrusion.

The products are particularly suitable for food packaging applications, especially for deep freezing applications.

Examples:

Heterophasic polymers:

[0027] The heterophasic polymers were produced in a two step process. In the first stage a random propylene/ethylene copolymer was polymerised (polymerisation in liquid propylene) and in the second stage a propylene/ethylene rubber was polymerised. The ratio between the propylene/ethylene random copolymer and the propylene/ethylene rubber was 92:8.

[0028] For visbreaking from the basic melt flow rate to a melt flow rate of about 10 - 15 g/10min Di-tertiary-butylperoxide was used.

The compositions and the additives were compounded in a twin screw extruder at a temperature of 250°C. The strands were quenched in cold water and pelletized.

[0029] The characteristics of the heterophasic polymers are given in table 1.

Table 1

	MFR2	XCS	C2	MFR2	XCS	C2	i..V.	C3/XCS
	matrix	matrix	matrix	total	total	total	XCS	
polymer	[g/10']	[wt%]	[mol%]	[g/10']	[wt%]	[mol%]	[ml/g]	[wt%]
polymer 1	1.09	7.2	5.6	1.22	12.2	8.5	1.38	66.0
polymer 2	1.13	6.7	6.3	1.27	12.0	9.8	1.65	65.0
polymer 3	1.13	6.7	6.3	1.19	12.1	9.2	1.59	66.0
polymer 4	1.05	6.6	6.0	1.12	13.3	8.4	1.70	68.5

Table 1 (continued)

	MFR2	XCS	C2	MFR2	XCS	C2	i.V.	C3/XCS
	matrix	matrix	matrix	total	total	total	XCS	
polymer	[g/10']	[wt%]	[mol%]	[g/10']	[wt%]	[mol%]	[ml/g]	[wt%]
MFR2 matrix: melt flow rate acc. ISO 1133 of phase (1)								
XCS matrix: xylene cold soluble fraction of phase (1)								
C2 matrix: ethylene content (randomly incorporated) of phase (1)								
MFR2 total: melt flow rate acc. ISO 1133 of the heterophasic system (phase 1+2)								
XCS total: xylene cold soluble fraction of the heterophasic system (phase 1+2)								
C2 total: total ethylene content of the heterophasic system (phase 1+2)								
i.V./XCS: intrinsic viscosity of xylene cold soluble fraction (indication of the molecular weight of the propylene/ethylene rubber - phase 2)								
C3/XCS: propylene content of xylene cold soluble fraction								

[0030] The polymers were mixed with conventional additives (0.05% Irgafos 168, 0.05% Irganox 1010, 0.1 Ca-steарат, 0.06% Glycerol monostearate, 0.18 % Millad 3988) in an intensive mixer (Henschel mixer) for 20 seconds.

Examples 1 - 4:

[0031] Polymers 1 - 4 of table 1 (component a) were mixed with 5% Exact 2M048, a commercial metallocene catalyst based polyethylene grade of MFR(190°C, 2.16 kg) 10 g/10min, density 902 g/cm³; DexPlastomers (component b)) was added. For visbreaking from the basic melt flow rate to a melt flow rate of about 10 - 15 g/10min Di-tertiary-butylperoxide was used.

The compositions and the additives were compounded in a twin screw extruder at a temperature of 250°C. The strands were quenched in cold water and pelletized.

Injection molded test bars were produced and the notched impact strength according to ISO 179 was measured.

[0032] For determining optical properties, especially transparency and haze injection molded plaques (60*60*2mm) were produced. The optical properties were measured according to ASTM D-1003-92.

Comparative examples 1- 4:

[0033] Heterophasic polymers of table 1 were used as comparative compounds.

Impact strength and optical properties were determined as described.

[0034] The results are given in table 2.

Table 2

			MFR	NIS/+23°C	IS/-20°C	haze
example	polymer	modifier	[g/10']	179 1eA/+23°C	179 1eU/-20°C	[%]
				[kJ/m ²]	[kJ/m ²]	
example 1	polymer 1	5% Exact 2M048	12.7	11.6	77.5	28.0
example 2	polymer 2	5% Exact 2M048	12.4	13.2	131.7	39.4
example 3	polymer 3	5% Exact 2M048	12.5	11.8	125.9	38.5
example 4	polymer 4	5% Exact 2M048	12.0	11.1	130.3	43.5
comp. Example 1	polymer 1		13.8	9.4	62.9	36.0
comp. Example 2	polymer 2		13.6	10.5	88.9	54.0
comp. Example 3	polymer 3		13.4	9.3	75.8	53.6
comp. Example 4	polymer 4		13.0	8.8	70.4	60.6

Examples 5 - 6:

[0035] Selected heterophasic polymers of table 1 (component a) were mixed with 5% Borealis CA9150 (commercial available LDPE grade of MFR(190°C, 2.16 kg) 15 g/10min, density 915 g/cm³, (component b)).

5 Comparative example 5 and 6 were prepared without adding component b).

The compositions were treated as described above, impact strength and optical properties were determined as described above.

[0036] The results are given in table 3.

Table 3

			MFR	NIS/+23°C	IS/-20°C	haze
example	polymer	modifier	[g/10']	179 1eA/+23°C	179 1eU/-20°C	[%]
				[kJ/m ²]	[kJ/m ²]	
example 5	polymer 2	5% Borealis CA 9150	13.5	10.5	108.3	40.8
	example 6	polymer 4	12.5	10.0	115.8	44.2

Claims

1. Polyolefin compositions with good impact strength and transparency comprising

a) 85 - 98 wt% based on the total weight of the composition of a heterophasic propylene/α-olefin copolymer comprising a polymer or copolymer of propylene and an α-olefin with 0-15 mol% of the α-olefin as matrix polymer and a propylene/α-olefin rubber copolymer comprising 20 -80 mol% of the α-olefin and
 b) 15 - 2 wt% based on the total weight of the composition of an ethylene homopolymer or an ethylene/α-olefin copolymer, the α-olefin in the ethylene copolymer having 4 - 10 carbon atoms, the ethylene homo- or copolymer having a density lower than 0,925 g/m³.

2. Polyolefin compositions according to claim 1, comprising

a) 90 - 97 wt% of a heterophasic propylene/α-olefin copolymers and
 b) 10 - 3 wt% of an ethylene homopolymer or an ethylene/α-olefin copolymer.

3. Polyolefin compositions according to one of claims 1 to 2, wherein the matrix polymer of the heterophasic polypropylene/α-olefin copolymer is a propylene/ethylene copolymer and the phase 2 polymer is a propylene/ethylene rubber.

4. Polyolefin compositions according to one of the claims 1 to 3 wherein the ratio of the matrix polymer to phase 2 polymer is about 97:3 to 80:20.

5. Polyolefin compositions according to one of the claims 1 to 4 wherein component b) is selected from the group of low density ethylene homopolymers and a metallocene based ethylene/α-olefin copolymers.

6. Polyolefin compositions according to one of the claims 1 to 5, wherein the ethylene content of the polyolefin composition is up to 15 mol%.

7. Polyolefin compositions according to one of the claims 1 to 6, wherein the melt flow rate of the polymer composition is 0.1 - 200g/min, preferably 0.2 - 50g/10 min, most preferably 0.5-20 g/min.

8. Polyolefin compositions according to one of the claims 1 to 7 further comprising conventional additives and/or stabiliser and/or fillers.

9. Process for producing polyolefin compositions according to one of the claims 1 to 8 , wherein the heterophasic polymer of component a) is produced in a multi stage process and mixed with the ethylene homopolymer or the

- ethylene/α-olefin copolymer.
10. Process according to claim 9, wherein components a) and b) are mixed by melt blending in the presence or in the absence of peroxides.
- 5
11. Use of the polymer compositions of one of the claims 1 to 8 for producing products for packaging applications by injection moulding, compression moulding, blow moulding, extrusion (film-, sheet-, pipe-, tube-, profile extrusion), film blowing, and thermoforming.

10

15

20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 00 12 6051

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X,D	EP 0 593 221 A (MITSUBISHI PETROCHEMICAL CO) 20 April 1994 (1994-04-20) * example 19 * ---	1-11	C08L53/00 C08L23/10
X	EP 0 714 923 A (SHOWA DENKO KK) 5 June 1996 (1996-06-05) * page 4, line 13; example 14 * ---	1-7, 9-11	
X	EP 0 844 281 A (JAPAN POLYCHEM CORP) 27 May 1998 (1998-05-27) * page 7, line 29; example 3 * ---	1-5, 7-11	
X	US 5 331 047 A (GIACOBBE JAMES) 19 July 1994 (1994-07-19) * page 3, line 31; example 4 * -----	1-3, 5, 7, 9-11	
TECHNICAL FIELDS SEARCHED (Int.Cl.7)			
C08L			
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	20 April 2001	Schmidt, H	
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 12 6051

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

20-04-2001

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 0593221	A	20-04-1994	DE	69320135 D	10-09-1998
			DE	69320135 T	10-12-1998
			JP	6192500 A	12-07-1994
			US	5391618 A	21-02-1995
EP 0714923	A	05-06-1996	AU	705455 B	20-05-1999
			AU	3790395 A	30-05-1996
			CA	2162946 A	22-05-1996
			CN	1128767 A	14-08-1996
			DE	69517771 D	10-08-2000
			DE	69517771 T	23-11-2000
			JP	3002119 B	24-01-2000
			JP	8198922 A	06-08-1996
			US	5703172 A	30-12-1997
			US	5804665 A	08-09-1998
			JP	3034452 B	17-04-2000
			JP	8198923 A	06-08-1996
EP 0844281	A	27-05-1998	JP	10152597 A	09-06-1998
			US	6015857 A	18-01-2000
US 5331047	A	19-07-1994	AT	156169 T	15-08-1997
			AU	667764 B	04-04-1996
			AU	5520694 A	25-08-1994
			CA	2115534 A	18-08-1994
			CN	1097432 A, B	18-01-1995
			DE	69404495 D	04-09-1997
			DE	69404495 T	29-01-1998
			EP	0611801 A	24-08-1994
			FI	940752 A	18-08-1994
			JP	7026084 A	27-01-1995
			MX	9401189 A	31-08-1994
			NO	940552 A	18-08-1994
			RU	2124535 C	10-01-1999
			US	5453318 A	26-09-1995